Biobased Aromatic-Aliphatic Polyols from Cardanol by Photochemical Thiol-ene Reaction

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ABSTRACT: Biobased aromatic-aliphatic polyols were previously synthesized from a thermal thiol-ene reaction of propoxylated cardanol with 2-mercaptoethanol (ME) in the presence of azobisisobutyronitrile (AIBN) as a radical initiator. Cardanol used for this purpose was obtained as a dark-brown liquid (Gardner Color Reference ~18). The photochemical thiol-ene reaction can also be used to prepare aromatic-aliphatic polyols by employing cardanol. Via the photochemical thiol-ene reaction, 2-mercaptoethanol was added successfully to C=C double bond of cardanol, suggesting that phenolic group may not play an inhibitory role in the radical thiol-ene reaction. However, we preferred to alkoxylate the phenolic hydroxyl group of cardanol, which is much more reactive with isocyanates than phenolic hydroxyls, to generate a new aliphatic hydroxyl group. Furthermore, the functionality of polyols was also improved by two methods: 1) using 1-thio-glycerol instead of 2-mercaptoethanol and 2) using alkoxylated cardanol with glycidol (Cardanol-GLY) instead of propoxylated cardanol (Cardanol-PO). These polyols were then used in preparation of rigid polyurethane foams that can be useful in various applications such as insulation of freezers, pipes and storage tanks in food and chemical industries.

KEYWORDS: Cardanol, photochemical reactions, thiol-ene reaction, 2-mercaptoethanol, 1-thio-glycerol

1 INTRODUCTION

Previously, we reported the preparation of biobased aromatic-aliphatic polyols by thermal thiol-ene reaction of propoxylated cardanol with 2-mercaptoethanol in the presence of radical initiator, AIBN (azobisisobutyronitrile) [1]. Propoxylation was carried out by employing a dark red-brown cardanol, Cardolite NX-2021 (Gardner Color Reference ~18). The synthesized polyols led to rigid polyurethane foams with excellent physical-mechanical properties. We utilized a much lighter-colored cardanol, Cardolite NX-2023 (Gardner Color Reference ~5), obtained from Cardolite Corporation [2], for preparation of polyols by photochemical thiol-ene reaction. However, the cardanol we used was a mixture of species. The phenolic ring with a chain of 15 carbons at the meta position, contains one, two, or three double bonds. It has, on average, 2.1 double bonds/mol.

Initially, polyols were prepared photochemically by using propoxylated cardanol and 2-mercaptoethanol (ME), in a similar way as in thermal thiol-ene reactions. Later, the functionality of polyols was increased by alkoxylation of cardanol with glycidol in the presence of a tertiary amine as a catalyst [3]. Thus, one phenolic group was transformed into two aliphatic hydroxyl groups, which reacted easily with aromatic isocyanates. We also adopted another method to obtain highly functional polyols by replacing 2-mercaptoethanol with another hydroxyalkyl mercaptan, 1-thio-glycerol (TG). By using 1-thio-glycerol, one double bond can be transformed into thio-ether containing two hydroxyl groups (new structure). Thus, synthesized polyols obtained from the reaction of alkoxylated cardanol with 2-mercatoethanol (ME) and 1-thio-glycerol (TG) were transformed into rigid polyurethane foams. The rigid polyurethane foams were characterized using standard methods.

2 EXPERIMENTAL

2.1 Materials

Cardanol (Cardolite NX-2023), which was supplied by Cardolite Corporation, is a light-colored yellow-brown liquid (Gardner Color 5), with iodine value of 220 g I_2/100 g. Propylene Oxide (PO), 99.8%, Glycidol,

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96%, and 1,1,3,3-tetramethyl guanidine (TMG), 99%, (the catalyst for alkoxylation of phenolic group) were purchased from Acros Organics. Chevron Phillips Chemical Company LP in Bartlesville, Oklahoma, supplied 2-mercaptoethanol (ME), 99.5% (trade name BME), a colorless liquid with a sulfur content of 41.0% and thiol equivalent weight (EW) of 39.1. Both 1-thioglycerol (TG), 95%, and 2-Hydroxy-2-methylpropiophenone (photoinitiator), 96%, were purchased from TCI America. Jeffol SG-360, a sucrose-glycerol polyether polyol with hydroxyl number 360 mg KOH/g, was obtained from Huntsman Corporation. Silicone surfactant Tegostab B 8404 and Niax™ A-1 catalyst bis(2-dimethylaminoethyl) ether were purchased from Evonik Industries Inc. and Momentive Performance Materials Inc., respectively. DABCO T-12 (dibutyltin dilaurate) was obtained from Air Products and Chemicals Inc. Rubinate M, a polymeric MDI having a 31% NCO and functionality of 2.7 (EW=135) was obtained from Huntsman Corporation.

2.2 Methods

Hydroxyl numbers and acid values of polyols were determined by the *p*-toluenesulfonyl isocyanate method (ASTM 1899) and by titration with 0.1 N NaOH in a toluene-isopropanol mixture (ASTM D4662), respectively. Viscosity was measured at 25 °C using an AR 2000ex rheometer (TA Instruments). Iodine value (IV) was determined by the Hanus method and is expressed as g I_2/100 g.

A size-exclusion chromatography (SEC) system, consisting of a Waters 515 pump (Waters Corp., Milford, MA), with a set of five Phenogel™ columns from Phenomenex Inc. (Torrance, CA) covering a molecular weight range of 100 to 5×10^5, was used for assessing molecular weight and molecular weight distribution. Calibration was carried out using a range of triglycerides, diglycerides, and fatty acid esters of similar structure.

A Fourier transform infrared (FTIR) spectrometer (IRAffinity-1 from Shimadzu) was employed to analyze the functional groups of polyols. NMR spectra were obtained from a Bruker Avance DPX-300 spectrometer, 300 MHz, with a 5 mm broadband probe using deuterated chloroform as a solvent.

Compressive properties were measured using an Instron® (model 3367) device, according to ASTM 1621. Closed-cell content of foams was measured by HumiPyc™ Volumetric and RH Analyzer from InstruQuest Inc. (Coconut Creek, FL), according to ASTM D2856. DSC measurements were performed using a differential scanning calorimeter (model Q100 from TA Instruments, New Castle, DE) in nitrogen (50 mL/min flow), at a heating rate of 10 °C/min from –80°C to 200°C.

2.3 Polyols Synthesis

2.3.1 *Propoxylation of Cardanol*

Cardanol was propoxylated by reacting cardanol with propylene oxide in the presence of TMG (1,1,3,3-tetramethylguanidine) in a metallic Parr reactor at 105–110 °C and 3–4 bars [1]. The reaction mixture was stirred continuously for 2 hours. The traces of unreacted propylene oxide were removed by vacuum distillation (~50–60 mm Hg) for about an hour at 100–105 °C. Thus, obtained propoxylated cardanol is a liquid with low viscosity.

2.3.2 *Alkoxylation of Cardanol with Glycidol*

The phenolic group of cardanol was blocked by alkoxylation with glycidol, using TMG as a catalyst, at around 105–110 °C [1]. All reagents—cardanol, glycidol and the catalyst—were charged in a metallic Parr reactor. The reactor was purged with nitrogen several times for inert atmosphere. Stoichiometric ratio of 1.1/1 = [glycidol]/[OH] was used. After a roughly three-hour reaction and vacuum distillation for purification, the product obtained was a slightly viscous, light-yellow liquid.

2.3.3 *Photochemical Thiol-ene Reaction*

Alkoxylated cardanol (prepared from cardanol and propylene oxide or glycidol), hydroxyalkyl mercaptans (2-mercaptoethanol or 1-thioglycerol), and photoinitiator (2-Hydroxy-2-methylpropiophenone) were mixed in a 500 mL glass vial (Ace Glass). In addition, 25–30 wt% tetrahydrofuran (THF) was added to the reaction mixture. During the course of photochemical thiol-ene reactions, the reaction mixture became very viscous, and it was not possible to stir mechanically. Use of solvent in the reaction mixture eased stirring the mixture efficiently. THF was chosen as a solvent because it is transparent to UV light. The reactor was then placed in a closed cabinet to avoid exposure of UV light to eyes. The reaction mass was stirred continuously for about 3 hours under a powerful 450 watt UV lamp. Since the thiol-ene reaction is exothermic, the lamp and the reaction mixture were cooled down using a thermostat prior to opening the cabinet. A 1/1 ratio of water/ethylene glycol at 30–32 °C was used in the cooling system. After completion of the reaction, solvent was removed by vacuum distillation at 60–80 °C, using a medium vacuum (60–70 mm Hg), followed by a high vacuum (2–5 mm Hg).

2.4 Preparation of Rigid PU Foams

Rigid polyurethane foams were prepared by using a mixture of cardanol polyols (50%) with a sucrose polyol Jeffol 360 (50%) and also by using 100% cardanol polyols. Polyols, silicone surfactant, amine catalyst, tin catalyst and water were mixed first in a polystyrene cup to prepare polyol Component A. Rigid polyurethane foams were then prepared by vigorously mixing polyol Component A with polymeric MDI (Rubinate M) at 3000 rotations/minute. Cream time, rise time and tack-free time were recorded to characterize the foaming process. These foams were characterized using standard methods after one week of maturation at room temperature.

3 RESULTS AND DISCUSSION

Thiol-ene reaction is the anti-Markovnikov addition of thiol group of mercaptans to C=C double bond. Photochemical thiol-ene reaction is initiated by UV light (see Scheme 1) in the presence of a photoinitiator [4–11].

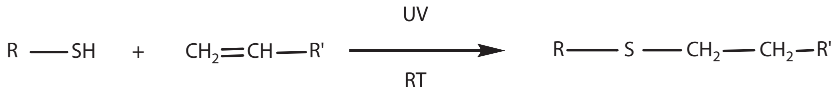
Photochemical thiol-ene reaction occurs via radical mechanism. At first, the reaction is initiated by formation of radicals in the presence of UV light (see Scheme 2). The radical reacts with thiol group to generate thiyl radical. Then the thiyl radical is added to the C=C double bond of the reaction system, resulting in carbon radical. This radical again transfers to the thiol group and generates new thiyl radical [1]. Thus, the radical reaction continues.

Cardanol (3-n-pentadecadienyl phenol) is a mixture of phenols containing a chain of 15 carbons at the meta position with a double bond (25–36%), two double bonds (16–22%) and three double bonds (30–41%) [12–14]. Cardanol is one of the very interesting aliphatic-aromatic biobased raw materials for preparation of polyols and polyurethanes [15–27]. It can be transformed into valuable new polyols by reaction with phenolic ring (alkoxylation, Mannich reaction [16–18]). Furthermore, photochemical thiol-ene reaction between hydroxyalkyl mercaptans and C=C double bond of C15 chain also resulted in new polyols for preparation of rigid polyurethane foams.

The phenolic group is known to be a radical inhibitor; therefore, the phenolic group needs to be blocked by alkoxylation prior to use in thiol-ene reaction. However, to our surprise, photochemical thiol-ene reaction of cardanol (used without blocking phenolic group) and ME[15] resulted in the successful addition of ME to the C=C double bond of the C15 chain (see Figure 1). This observation demonstrates that the phenolic hydroxyl group has a minimal effect on the radical transfer reaction, forming thiyl radicals preferentially over aryloxy radicals.

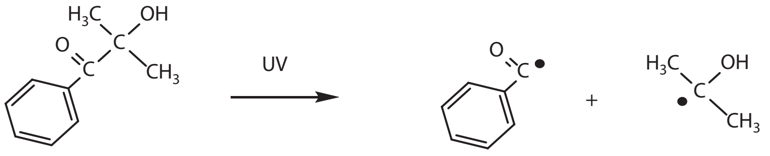
The ^{1}H NMR of cardanol and Cardanol-ME also suggests that thiol-ene reaction occurred. The ^{1}H NMR of cardanol shows a presence of methyl group at 0.89 ppm and methylene groups at 1.31 ppm, 1.58 ppm, 2.03 ppm, 2.55 ppm and 2.80 ppm (Figure 2). The peaks at the range 4.96–5.09 ppm and a multiplet at around 6.25 ppm correspond to vinyl protons of terminal C=C double bonds. Peaks at around 5.35 ppm show the presence of internal vinyl protons. Aromatic protons are observed at 6.66 ppm, 6.77 ppm and 7.14 ppm, respectively. These results show that the cardanol is a mixture of compounds which may contain one or two internal double bonds and a terminal double bond. The lack of the peaks at the range 4.96–5.09 ppm and a multiplet at 6.25 ppm in the ^{1}H NMR of Cardanol-ME show the thiol-ene reaction between cardanol and ME; however, the internal double bonds still remained. A methylene peak at 3.74 ppm is due to the addition of ME to C=C bonds of cardanol.

However, we preferred alkoxylation of the phenolic group due to the low reactivity of phenols towards isocyanates. The phenolic group of cardanol was alkoxylated with propylene oxide or glycidol to obtain more reactive aliphatic hydroxyl groups. At the same time, propoxylation of the phenolic group also increased



$$R-SH + CH_2{=}CH-R' \xrightarrow[RT]{UV} R-S-CH_2-CH_2-R'$$

Scheme 1 General thiol-ene reaction.



Scheme 2 2-Hydroxy-2-methylpropiophenone (photoinitiator) splits into two radicals.

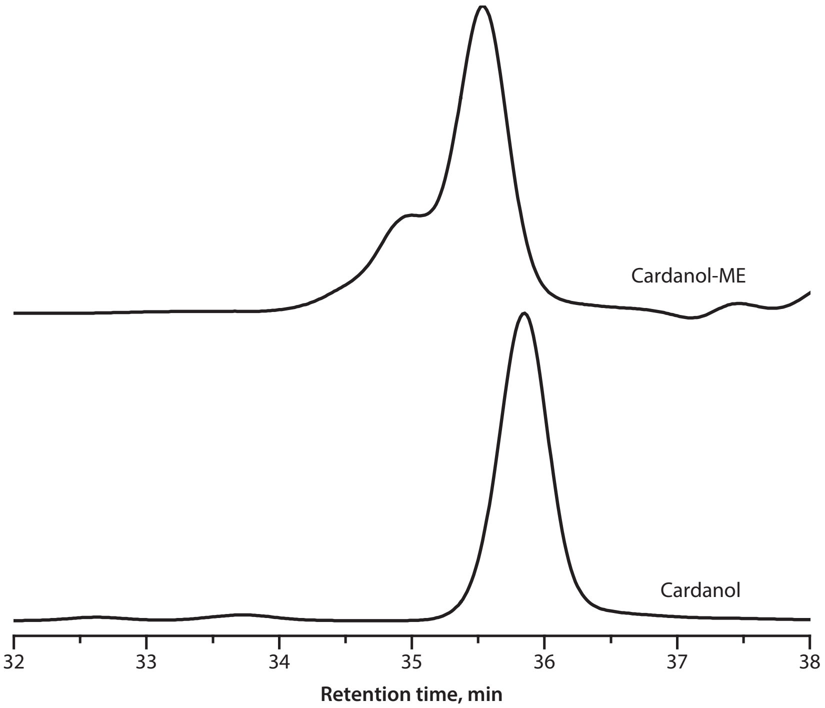


Figure 1 Size exclusion chromatogram of cardanol and cardanol reacted by ME (Cardanol-ME).

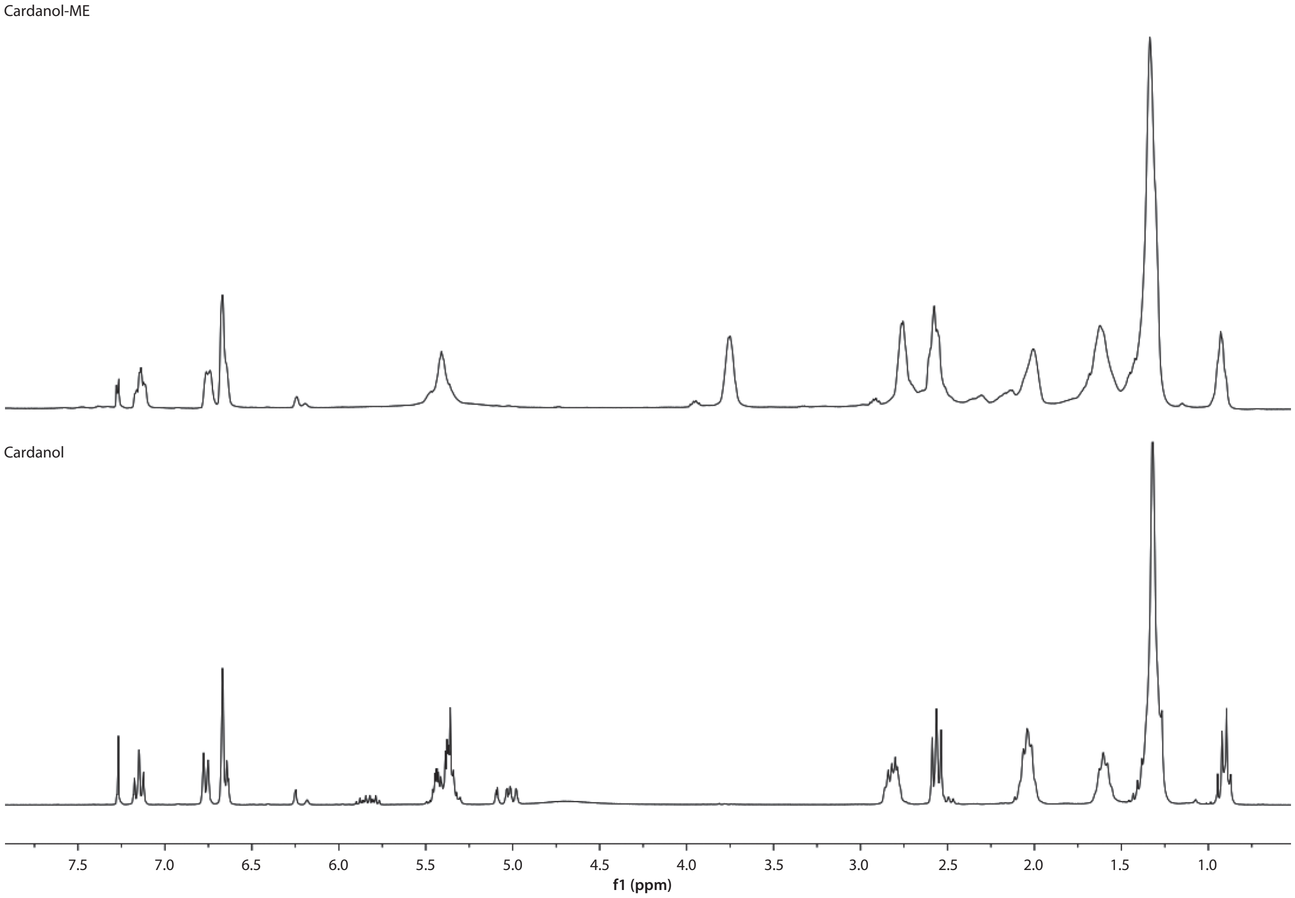


Figure 2 ^{1}H NMR overlay of Cardanol and Cardanol-ME.

the functionality of the resultant polyol when used in thiol-ene reaction. Thus, alkoxylation of phenolic hydroxyl group[3] is found to be more favorable for preparation of polyols containing average functionality 3-4 hydroxyl groups/mol.

Propoxylation of cardanol transformed the phenolic hydroxyl group into hydroxyl propyl ether (see Scheme 3). The product from the reaction of cardanol with glycidol is also presented in Scheme 4, the phenolic group being converted to a hydroxyalkyl ether containing two hydroxyl groups. The SEC (size-exclusion chromatogram) showed that cardanol completely reacted in alkoxylation, providing Cardanol-PO and Cardanol-GLY, respectively. A small peak at around 34.5 min is observed in the SEC of both Cardanol-PO and Cardanol-GLY, which could be due to the reaction of cardol present in the starting material, cardanol.

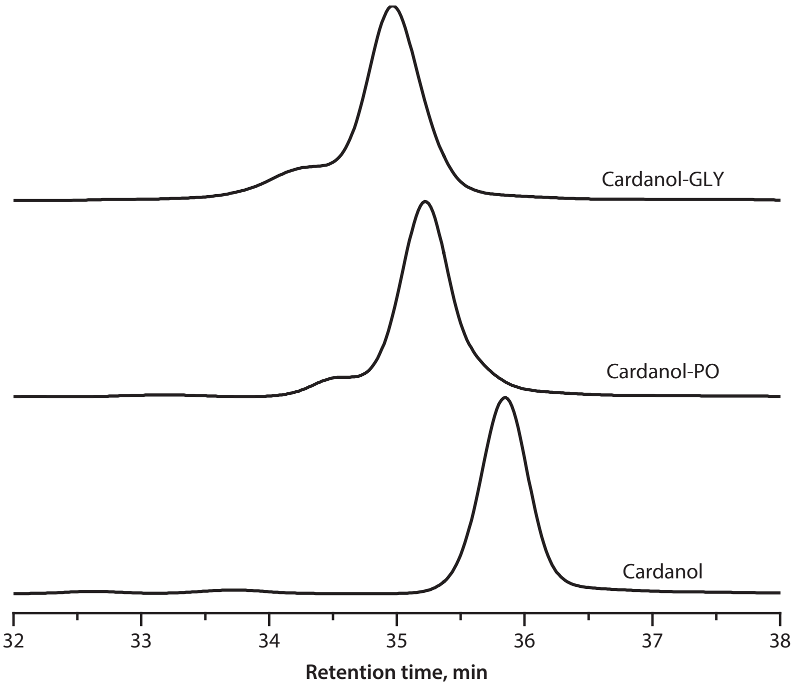
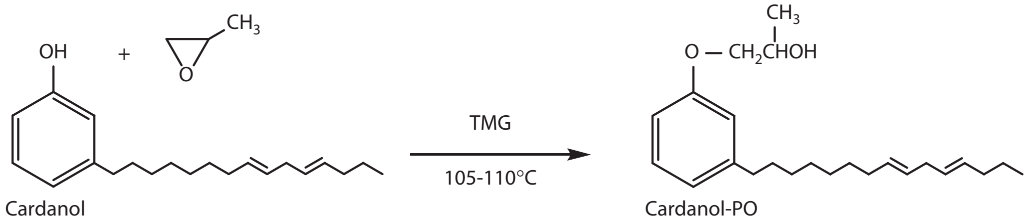
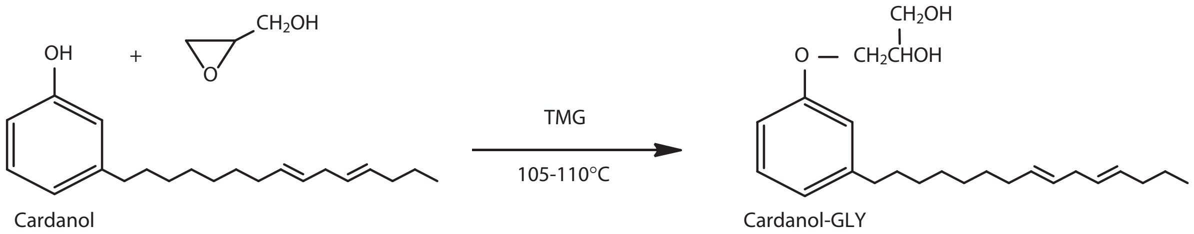


Figure 3 Size-exclusion chromatograms of cardanol alkoxylated with propylene oxide (Cardanol-PO) and with glycidol (Cardanol-GLY).



Scheme 3 Propoxylation of cardanol (Cardanol-PO).



Scheme 4 Alkoxylation of cardanol with glycidol (Cardanol-GLY).

Cardanol-PO and Cardanol-GLY were characterized before being employed in the thiol-ene reaction (see Table 1). Hydroxyl numbers of both Cardanol-PO and Cardanol-GLY were minimally higher than the theoretical values. Furthermore, these compounds are slightly basic, probably due to the presence of TMG, which was used as a catalyst for alkoxylation.

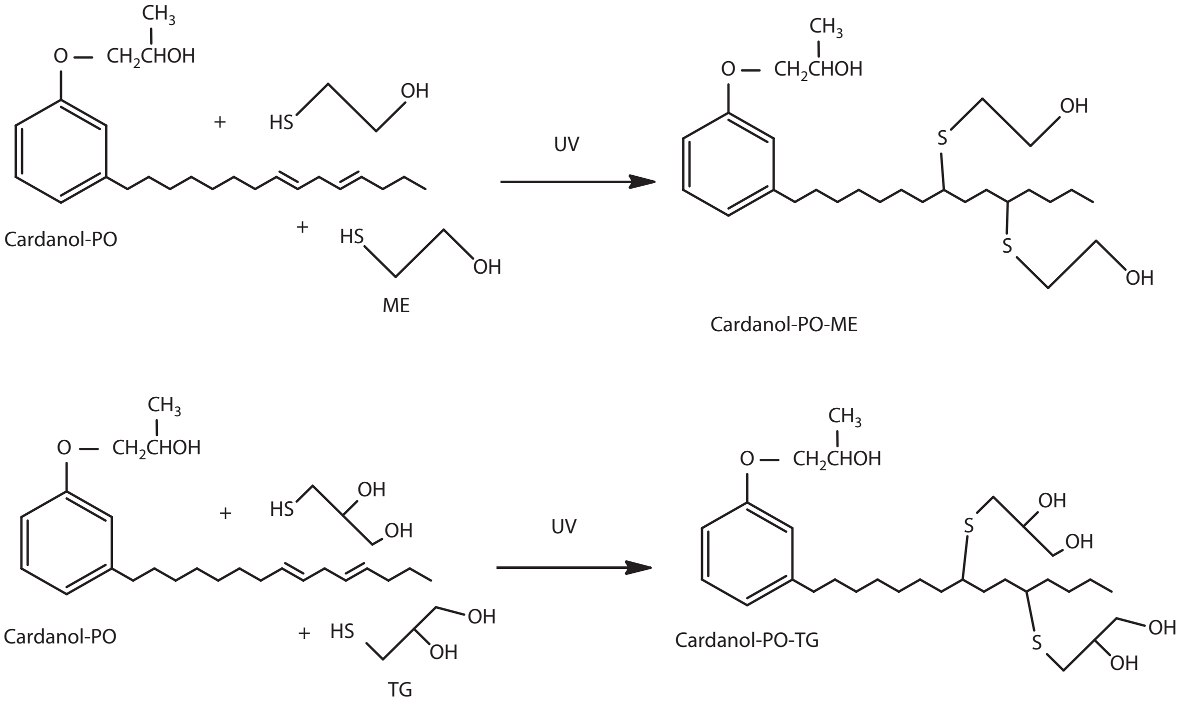
Since cardanol is a complex mixture with average functionality of roughly 2 double bonds/mol, hydroxyalkyl mercaptan could potentially react with either one, two, or even three C=C double bonds. Possible structures of polyols, Cardanol-PO-ME, and Cardanol-PO-TG, obtained from the photochemical thiol-ene reaction of Cardanol-PO with 2-mercaptoethanol (ME) and 1-thioglycerol (TG), are presented in Scheme 5.

Figure 4 shows the SEC of polyols obtained after thiol-ene reactions. The SEC of Cardanol-PO-ME suggests that both Cardanol-PO and ME used in photochemical thiol-ene reaction completely reacted, providing the desired polyols. However, the product is still a mixture, probably due to ME reacting with one, two, or three double bonds of the cardanol. The SEC of Cardanol-PO-TG also suggests a mixture of products resulting from a thiol-ene reaction of Cardanol-PO and TG. Furthermore, the shoulder peak at around 37 min could be due to the TG dimer formed during photochemical reaction.

Likewise, preparation of Cardanol-GLY-ME and Cardanol-GLY-TG containing 2 hydroxyalkyl mercaptan units/mol are shown in Scheme 6.

Table 1 Characteristics of alkoxylated cardanol (Cardanol-PO and Cardanol-GLY).

Characteristic	Cardanol-PO	Cardanol-GLY
Average molecular weight	358.00	374.00
Hydroxyl number (mg KOH/g)	165.72	323.31
Iodine value (g I_2/100 g)	144.18	127.03
Basicity (mg KOH/g)	2.70	1.68
Viscosity @ 25 °C (Pa.s)	0.0583	1.015
Density @ 25 °C (g/mL)	0.945	0.996



Scheme 5 Synthesis of polyols from photochemical thiol-ene reactions of Cardanol-PO with ME and with TG respectively.

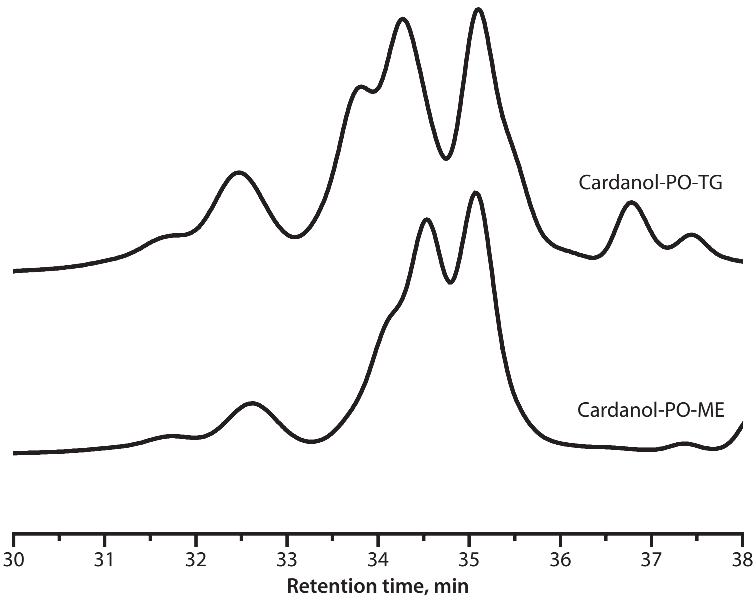
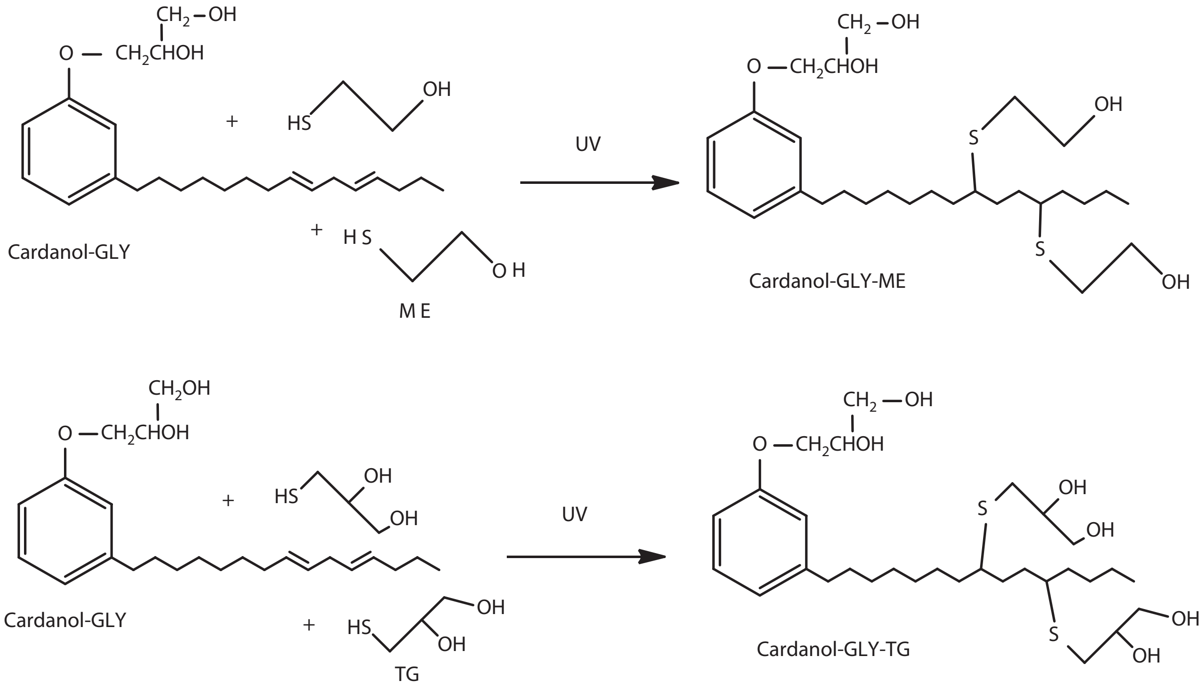


Figure 4 Size-exclusion chromatograms of aromatic-aliphatic polyols prepared from photochemical thiol-ene reactions of Cardanol-PO with ME (Cardanol-PO-ME) and with TG (Cardanol-PO-ME).



Scheme 6 Synthesis of polyols from photochemical thiol-ene reaction of Cardanol-GLY with ME and with TG.

The SEC of Cardanol-GLY-ME and Cardanol-GLY-TG also shows the thiol-ene addition to the C=C double bonds; however, the resulting polyols are a complex mixture as in the previous two polyols (see Figure 4).

These cardanol-based polyols are also characterized in Table 2.

High acid values of the resulting polyols are due to some unreacted thiol group, which shows incomplete addition to the double bond of a C15 chain. Hydroxyl

Table 2 Characteristics of cardanol-based polyols prepared by photochemical thiol-ene reaction.

Cardanol-based polyols	Viscosity (Pa.s)	Acid Value (mg KOH/g)	Hydroxyl number, (mg KOH/g)	M_n	M_w	M_w/M_n
Cardanol-PO-ME	0.8141	0.65	338.04	335.35	460.54	1.37
Cardanol-PO-TG	1.151	1.40	392.20	234.04	465.66	1.98
Cardanol-GLY-ME	8.565	15.39*	470.63	437.88	617.61	1.41
Cardanol -GLY-TG	5.050	14.37*	567.06	250.72	547.33	2.18

*high acid value

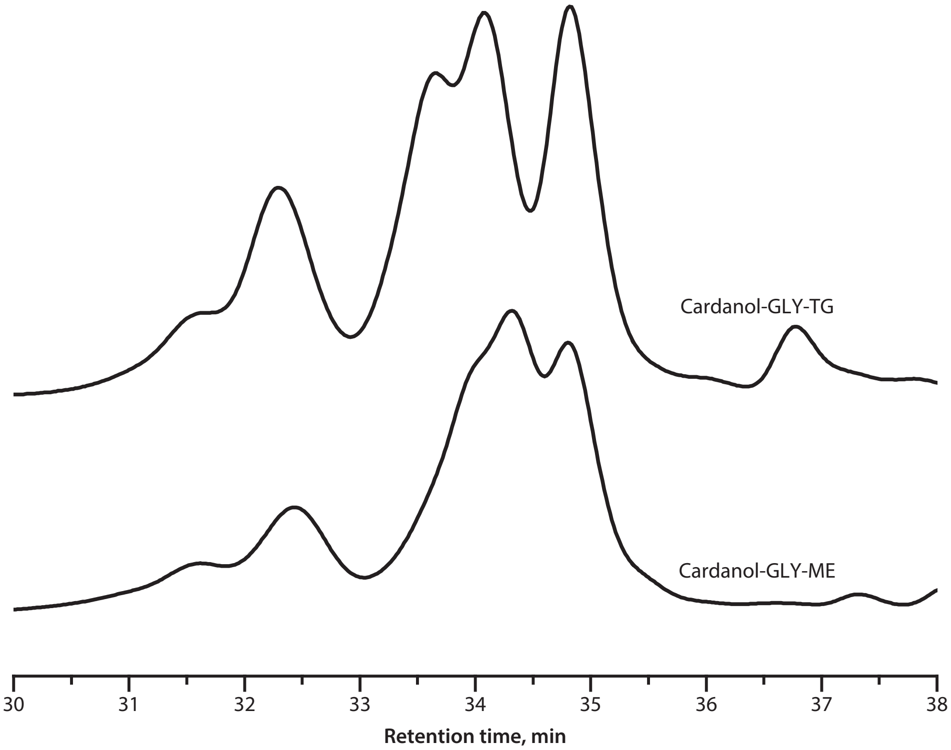


Figure 5 Size-exclusion chromatogram of aromatic-aliphatic polyol prepared from photochemical thiol-ene reaction of Cardanol-GLY with ME (Cardanol-GLY-ME) and with TG (Cardanol-GLY-TG).

numbers of these polyols are also slightly higher than the theoretical values, which also suggest the incomplete addition of thiol group to C=C bonds.

Furthermore, these polyols prepared from photochemical thiol-ene reactions including the starting materials were analyzed by ^{1}H NMR. As described previously, the ^{1}H NMR of cardanol suggests that the cardanol is a mixture of compounds which may contain one or two internal double bonds and a terminal double bond. A multiplet centered at 4.19 ppm of the ^{1}H NMR of cardanol-PO shows a presence of methine proton. Methylene protons observed in the range from 3.83–3.94 ppm suggest a reaction occurred between cardanol and PO. Furthermore, the absence of terminal double bonds (4.96–5.09 ppm and 6.25 ppm) in ^{1}H NMR of Cardanol-PO-ME shows the thiol-ene reaction carried out between Cardanol-PO and 2-mercaptoethanol. The peak at 5.38 ppm is still observed, which suggests the incomplete reaction with internal double bond. Nevertheless, the absence of a characteristic -SH peak, a triplet at 1.41 ppm in the ^{1}H NMR of Cardanol-PO-ME, also confirms the thiol-ene reaction. ^{1}H NMRs of other polyols, i.e., Cardanol-PO-TG, Cardanol-GLY-ME and Cardanol-GLY-TG, also suggest that thiol-ene reaction occurred, resulting in the desired polyols; however, some internal double bonds remain unreacted (Figure 7 and Figure 8). A triplet at around 1.41 ppm of the ^{1}H NMR of Cardanol-GLY-TG also suggests that unreacted TG is present in the polyols.

Figure 9 presents the FTIR spectrum of cardanol-based polyols prepared from photochemical thiol-ene reactions. A strong absorbance of the hydroxyl group is observed at around 3400 cm^{-1}, and aromatic rings can be found at 700–800 cm^{-1}. The absorbance for the C15 hydrocarbon chain (-CH$_2$ and -CH$_3$ groups) is in the range 1450 cm^{-1} and 2920 cm^{-1}, respectively. The absence of a double bond at 3010 cm^{-1} and –SH group at 2220 cm^{-1} is evidence of the addition of a thiol group to the C=C double bond.

Thus, we prepared four different polyols by using thiol-ene reaction photochemically. After careful analysis, these polyols were utilized for preparation of rigid polyurethane (PU) foams. Initially, 50% cardanol-based polyols were mixed with 50% sucrose polyether polyol Jeffol SG-360 (Formulation 1) to obtain PU foams. We also prepared rigid PU foams based solely on cardanol polyols (Formulation 2). Formulation 1 and Formulation 2, which were used for preparation of the mentioned rigid polyurethane foams, are presented in Table 3 (all the quantities in grams).

The foaming process using 50% cardanol-based polyols was rapid, with cream time of 9–10 seconds, rise time of 35–40 seconds, and tack-free time around 30–40 seconds. Characteristics of rigid polyurethane foams prepared from 50% cardanol polyols and 50% sucrose polyol Jeffol SG-360 are presented in Table 4. Densities of PU foams prepared from Cardanol-GLY-based polyols are higher compared to the foams prepared from Cardanol-PO-based polyols. All the foams possess very high closed-cell contents. Mechanical and thermal properties are also satisfactory.

Rigid polyurethane foams based exclusively on cardanol polyols (prepared by using Formulation 2), are characterized in Table 5. The foaming process was slightly more rapid (compared to the foams prepared from 50% cardanol-based polyols), with cream time of 9–10 seconds, rise time of 20–30 seconds, and tack-free time of 22–35 seconds. High reactivity during the foaming process may be due to the presence of TMG, a catalyst, used for alkoxylation of cardanol. TMG has a strong catalytic effect in reactions involving the –N=C=O group with the hydroxyl group and water

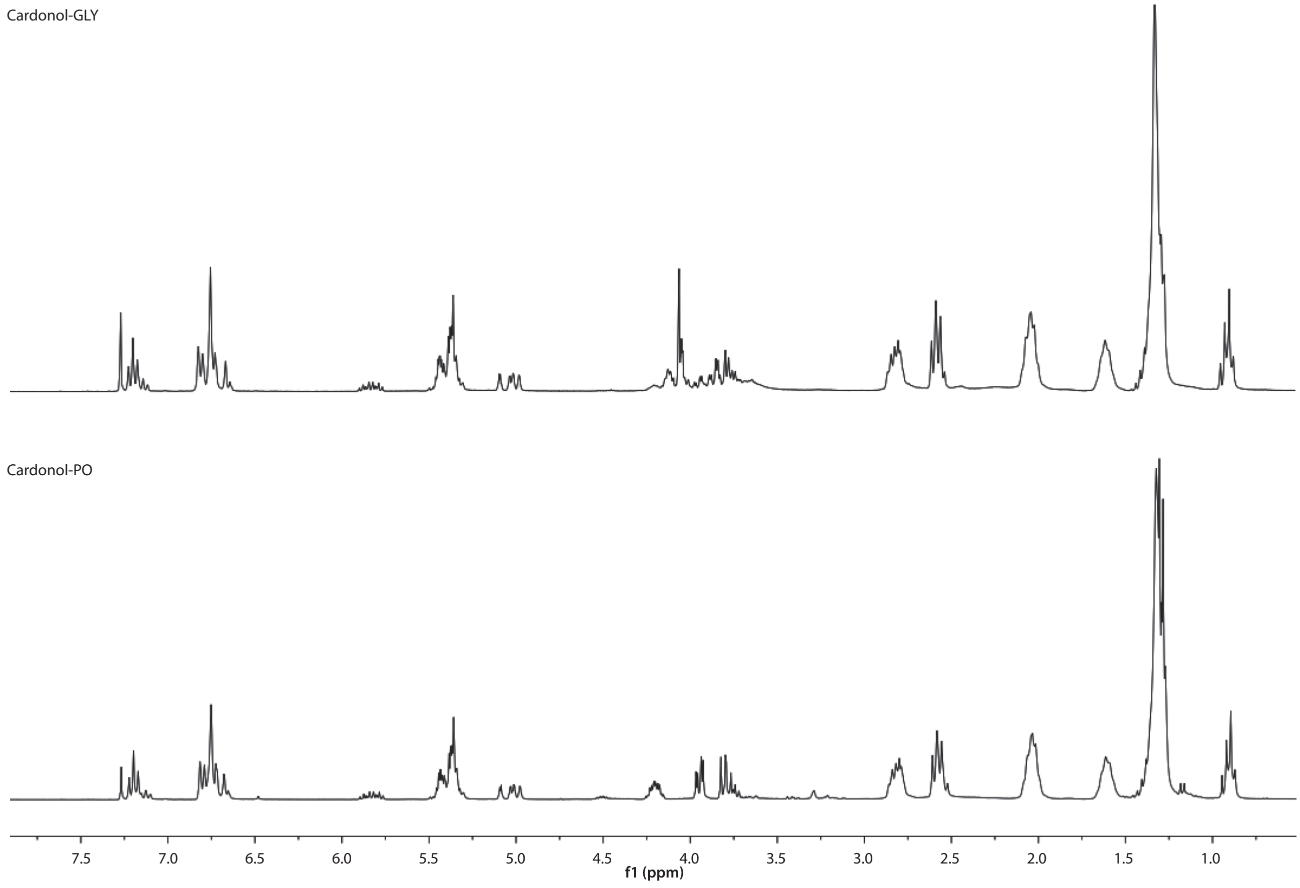


Figure 6 ^{1}H NMR overlay of Cardanol-PO and Cardanol-GLY.

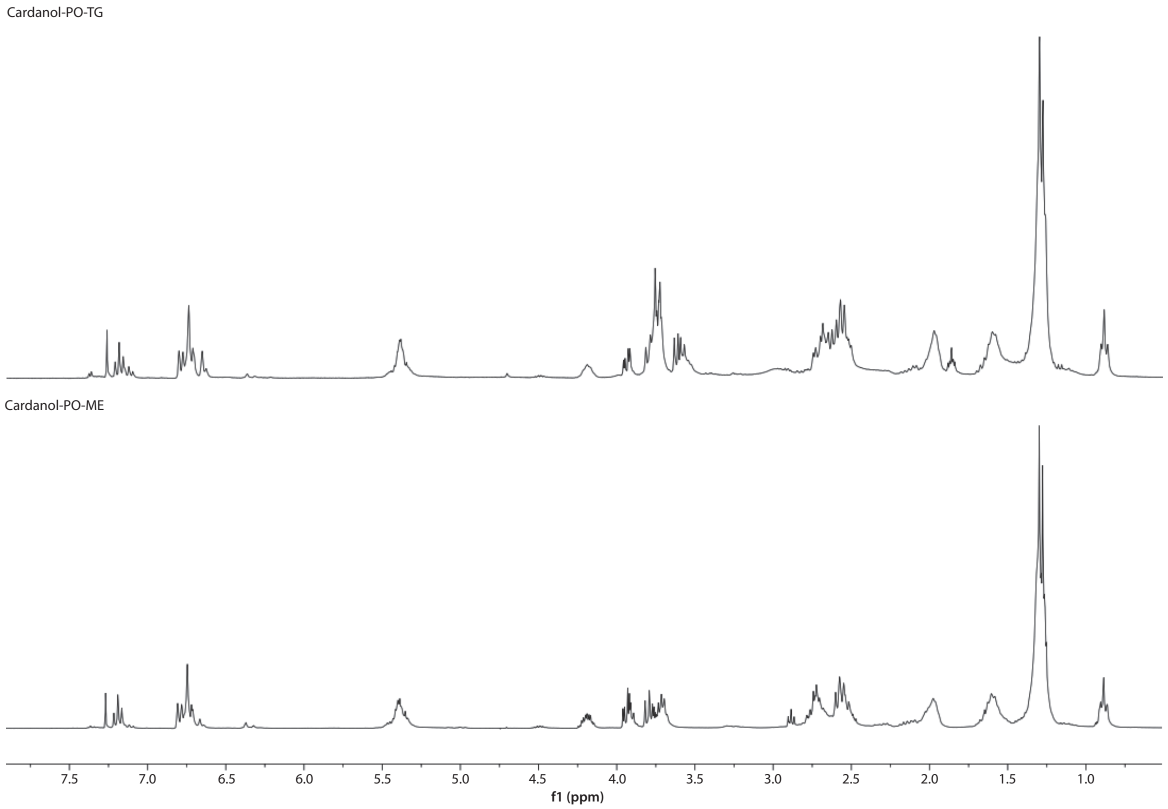


Figure 7 ^{1}H NMR overlay of Cardanol-PO-ME and Cardanol-PO-TG.

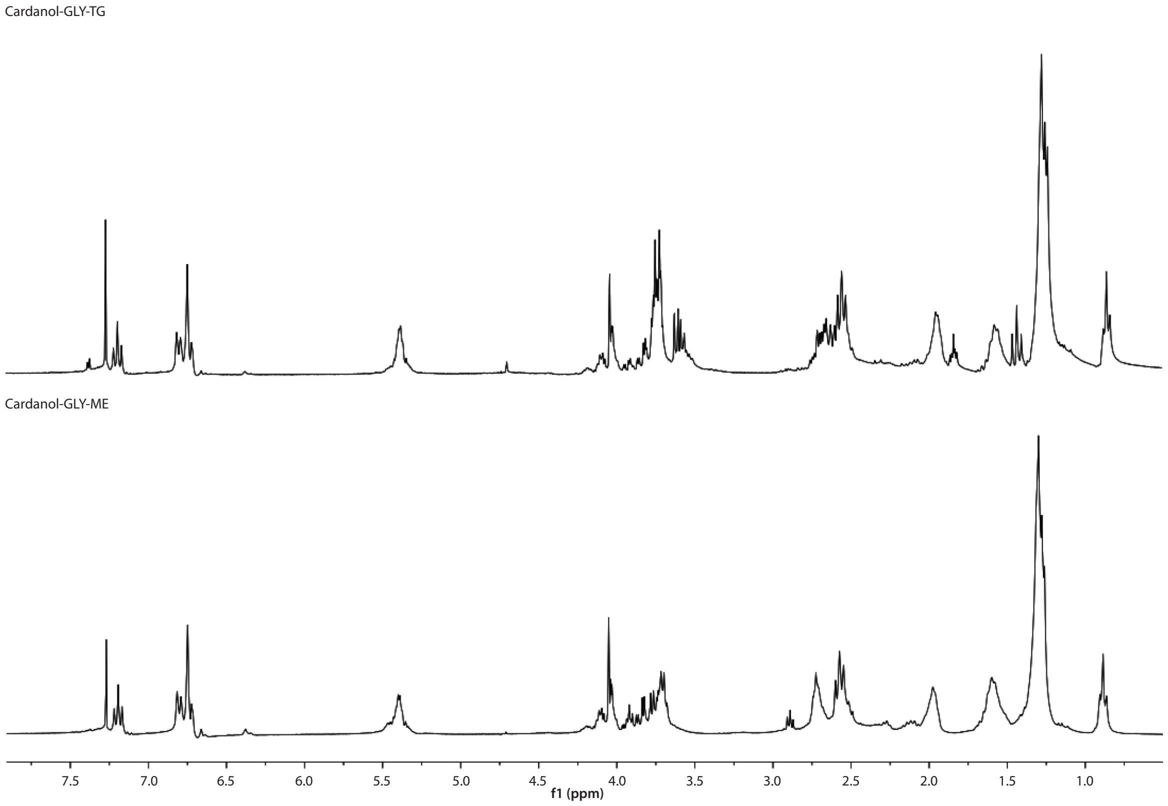


Figure 8 ^{1}H NMR overlay of Cardanol-GLY-ME and Cardanol-GLY-TG.

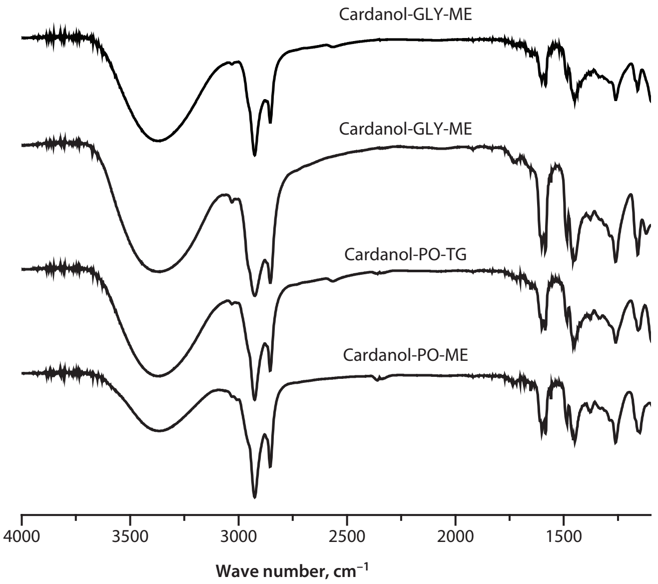


Figure 9 FTIR spectrum of cardanol-based polyols obtained from photochemical thiol-ene reactions.

Table 3 Preparation of rigid polyurethane foams.

Components	Formulation 1 (g)	Formulation 2 (g)
Cardanol polyol	10	20
Jeffol SG-300	10	–
Silicon B8404	0.4	0.4
Amine Niax A-1	0.12	0.12
Tin catalyst T-12	0.04	0.04
Water	0.8	0.8
Rubinate M, Index	105	105

Table 4 Characteristics of rigid PU foams from a mixture of cardanol polyols (50%) with sucrose polyether polyol Jeffol SG-360 (50%).

PU foam sample	Density, Kg/m³	Closed-Cell Content, %	Compression strength, Stress @10%, kPa	T_g (°C)
PU-Cardanol-PO-ME	32.0	94	253	48.16
PU-Cardanol-PO-TG	31.0	93	220	53.09
PU-Cardanol-Gly-ME	37.0	94	297	64.22
PU-Cardanol-Gly-TG	35.0	92	292	67.46

Table 5 Characteristics of rigid PU foams prepared from 100% cardanol-based polyols.

PU foam sample	Density, Kg/m³	Closed-Cell Content, %	Compression strength, Stress @10%, kPa	T_g (°C)
PU-Cardanol-PO-ME	32	92	101	44.03
PU-Cardanol-PO-TG	31	91	113	20.38
PU-Cardanol-GLY-ME	35	93	132	14.80
PU-Cardanol-GLY-TG	36	99	127	37.58

suggesting suitable application in "spray" PU foams. However, the high reactivity in the foaming process can be diminished by the removal of TMG via treatment with ion exchangers, acidic adsorbents, or simply by washing with water.

However, the use of 100% cardanol-based polyols leads to rigid polyurethane foams with lower compression strength. These results suggest that cardanol-based polyols (prepared from a photochemical thiol-ene reaction) perform better in a mixture with sucrose polyether polyol than when used as a sole polyol for preparation of rigid polyurethane foams.

4 CONCLUSIONS

New aromatic-aliphatic biobased polyols were prepared from a photochemical thiol-ene reaction at room temperature using 2-mercaptoethanol and 1-thio-glycerol with alkoxylated cardanol. The phenolic group of cardanol was converted to hydroxyalkyl group by alkoxylation with propylene oxide or with glycidol prior to use in the thiol-ene reaction. Thus, the phenolic group that was less reactive towards isocyanates was transformed into a more reactive hydroxyalkyl group. The synthesized polyols mixed with sucrose polyether polyols (1/1 w/w) provided rigid polyurethane foams, resulting in very good properties, including high closed-cell content and good compression strength. These cardanol polyol-based foams can be used in a variety of practical applications, such as insulation of freezers, pipes and storage tanks in food and chemical industries. Other possible applications may include thermal insulation for buildings or wood substitutes for packaging and flotation materials.

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